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Proton Transfer and Tautomerism in the 2AP–T and PC–G Base Pairs

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A. Ground State (S_0) PC-G Potential Energy Curves (Solution Phase)

Figure S1 Change in energy of the optimised ground state (S_0) geometry as a function of H_1 to N_1 distance of both the gas phase and solution phase PC-G base pair for the proton transfer process $N_3-(H)N_1$. Showing (top row of figures) the optimised solution phase Watson-Crick structure of PC-G, a local energy maximum ($LEnergy_{max}$) at $(H)N_1 = 1.347$ Å and a local energy minimum ($LEnergy_{min}$) at $(H)N_1 = 1.747$ Å with a $N_3(H)$ distance of 1.056 Å. The structure of PC-G TpII_{equi} produced by unrestricted geometry optimization in the gas phase (X on potential energy curve) and solution phase (X on potential energy curve) is shown as an inset figure on the plot.

B. Ground State (S_0) PC-G TpII_{equi} Structure (Solution Phase)

Figure S2 Gas (left figures) and solution phase (right figures) hydrogen bond distances for the PC-G TpII_{equi} structure in the ground state (S_0) computed at MP2/cc-pVDZ level. ΔE is the difference in energy between the gas phase and solution phase S_0 PC-G TpII_{equi} structures. Hydrogen bond lengths are given in Angstroms and dimer interaction energies are in kcal mol⁻¹.

C. Excited State (S_1) PC-G Potential Energy Curves (Solution Phase)

Figure S3 Change in energy of the optimised first excited state (S_1) as a function of distance of the solution phase PC-G base pair for the proton transfer process $N_3-(H)N_1$. Showing (top row of figures) the Watson-Crick structure of PC-G, the structure at $(H)N_1 = 1.342$ Å and a local energy minimum ($LE_{\min}$) at $(H)N_1 = 1.842$ Å. The structure of PC-G TpII_{equi} produced by unrestricted geometry optimization (X on potential energy curve) is shown as an inset figure on the plot. The symbol plotted represent the following electronic states: ■ $^1LE(\pi\pi^*)$ on PC.

Figure S4 Solution (left figures) and gas (right figures) phase $\text{LEnergy}_{\text{max}}$ structures of the PC-G TpI_{equi} S_1 optimised pyrrolocytosine-guanine geometries. Bond distances are in Angstroms.

D. PC–G TpII_{equi} Structure in Electronically Excited States (Solution Phase)

The vertical transition energies and energies of the optimised geometries of the first two excited states of Tautomer Base Pair I in solution phase are shown in Table S1.

Transition	Excitation			Emission		
	$\Delta E/\text{eV}$	f	Assignment	$\Delta E/\text{eV}$	f	Assignment
1	3.469	0.163	$^1\pi_{\text{PC}}^1\pi_{\text{PC}}^*$	3.449	0.159	$^1\pi_{\text{PC}}^1\pi_{\text{PC}}^*$
2	5.728	0.323	$^1\pi_{\text{PC}}^1\pi_{\text{PC}}^*$	5.466	0.421	$^1\pi_{\text{PC}}^1\pi_{\text{PC}}^*$

Table S1 Vertical excitation energies, oscillator strengths and assignments of the two lowest singlet vertical excited transitions and transitions of the optimised geometries of PC–G TpII_{equi} in solution phase. Calculations were performed at CIS/cc-pVDZ level using the PCM method with water as the solvent.

(a)

(b)

(c)

Figure S5 Optimised geometries, in plane and profile views, of the ground state (S_0) PC–G $\text{TpII}_{\text{equi}}$ pyrrolocytosine-guanine base pair in solution phase (computed at MP2/cc-pVDZ level) (a), with first (S_1) and second (S_2) electronic excited state geometries (b), and (c),

respectively (computed at CIS/cc-pVDZ). Bond distances are in Angstroms and dimer interaction energies are in kcal mol⁻¹.

Figure S6 Change in energy of the optimised ground state (S_0), the first excited state (S_1) and $S_0 \rightarrow S_1$ vertical transition energy from as a function of distance of the solution phase PC-G base pair for the double proton transfer process between $N_3-(H)N_1$ and $N_7(H)-O_6$. The structure of PC-G TpII_{equi} produced by unrestricted geometry optimizations at S_1 and S_0 , $\times$

and $\times$, respectively are shown as inset figures on the plot. The symbols plotted represent the following electronic states: $\bullet$ ground state; $\blacksquare$ $^1\text{LE}(\pi\pi^*)$ on PC.

E. Ground State (S_0) 2AP–T Potential Energy Curves (Solution Phase)

The potential energy curve of the transfer of the $N_2(H)$ proton from 2-aminopurine to thymine in the electronic ground state (S_0) is illustrated in Figure S7. Unfortunately, the geometries of these proton transfer structures had two or more negative frequencies identified by calculating the Hessian matrix, and so are not true minimum structures. However, the $N_2(H)$ proton transfer potential energy curve in solution phase is in good, qualitative agreement with the potential energy curve of the gas phase, for which true minimum structures were found during geometry optimisation.

Figure S7 Change in energy and dipole moment of the optimised ground state (S_0) geometry as a function of N_2 to H_2 distance of the solution phase 2AP–T base pair for the proton

S10

transfer process $\text{N}_2\cdot(\text{H})\text{--O}_2$. Showing the 2AP–T TpI_{equi} structure of 2AP–T, a local dipole maximum ($\text{LDipole}_{\text{max}}$) of $\text{N}_2\cdot(\text{H})$ at $1.325\text{\AA}$ and a local dipole minimum ($\text{LDipole}_{\text{min}}$) at $\text{N}_2\cdot(\text{H}) = 1.525\text{\AA}$ and a $(\text{H})\text{O}_2$ distance of $1.068\text{\AA}$.

F. Excited State (S_1) 2AP-T Potential Energy Curves (Solution Phase)

Figure S8 Change in energy of the optimised first excited state (S_1) as a function of distance of the solution phase 2AP-T base pair for the proton transfer process $N_2(H)-O_2$. Showing (top row of figures) the 2AP-T TpI_{equi} structure of 2AP-T, the structure at $N_2(H) = 1.307$ Å and a local energy minimum (LE_{min}) at $N_2(H) = 1.607$ Å. The structure of 2AP-T TpI_{equi} produced by unrestricted geometry optimization (x on potential energy curve) is shown as an inset figure on the plot.

Figure S9 Solution (left figures) and gas (right figures) phase $\text{LEnergy}_{\text{max}}$ structures of the S_1 optimised 2-aminopurine-thymine geometries. Bond distances are in Angstroms.

G. 2AP-T TpII_{equi} Structure in Electronically Excited States (Solution Phase)

Figure 10 Potential energy pathway for the double proton transfer process between $N_{1,-}(H)N_3$ and $N_{2,(H)}-O_2$ of the 2AP-T base pair in the solution phase. The structure of 2AP-T TpII_{equi} produced by unrestricted geometry optimizations at S_1 (X) is shown as an inset figure on the plot. The symbols plotted represent the following electronic states: ● ground state; ■ ${}^1LE(\pi\pi^*)$ on 2AP.